Models of Acid-Base Chemistry

Several models have been developed to classify, rationalize and predict the reactivity of acid-base pairs (or donor-acceptor pairs).

- **Arrhenius Model** – acids give hydrogen ions in aqueous solution and bases give hydroxide in aqueous solution

- **Brønsted-Lowry Model** – acids are hydrogen ion donors and bases are hydrogen ion acceptors

- **Lewis Model** – acids are electron pair acceptors and bases are electron-pair donors

- **Electrophile-Nucleophile Model** – acids are electrophilic reagents and bases are nucleophilic reagents

- **Lux-Flood Model** – acids are oxide ($O^{2-}$) acceptors and bases are oxide donors

- **Usanovich Model** – an acid-base reaction is a reaction leading to formation of a salt
Arrhenius Acid-Base Model

Acids form hydrogen ions in aqueous solution and bases form hydroxide in aqueous solution

\[ HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O \]

HCl(aq) $\rightarrow$ $H^+$ + $Cl^-$  acid

NaOH(aq) $\Rightarrow$ $Na^+$ + $OH^-$  base

- Good fundamental definition of acids and bases for aqueous solution
- Of limited use in non-aqueous solvents or the gas phase where dissociation doesn’t occur
- Also fails to capture analogous reactivity of substances that don’t dissociate into $H^+$ or $OH^-$, e.g., what do you do about NH$_3$?
**Brønsted-Lowry Model**

Acids release hydrogen ions and bases take up hydrogen ions

\[ HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \]

- **Conjugate acids and bases** – when an acid gives up a hydrogen ion, it forms the conjugate base

- Acid-base reactions always proceed to form the weaker acid/base pair

- The Brønsted-Lowry Model accommodates non-aqueous solvents and gas-phase reactions

\[ NH_4^+ + NH_2^- \xrightarrow{NH_3} 2NH_3 \]

\[ NH_4^+ \xrightarrow{NH_3} H^+ + NH_3 \]

\[ NH_2^- + H^+ \xrightarrow{NH_3} NH_3 \]
Solvent System Model

This model for acid-base reactivity was developed for solvents that can dissociate into cations (acid) and anions (base)

- The classic example is water:

\[
2H_2O \rightleftharpoons H_3O^+ + OH^- \\
\text{acid} \quad \text{base}
\]

- Now we can say that sulfuric acid is an acid because it increases the concentration of $H_3O^+$:

\[
H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^- \\
nH_3O^+ + OH^- \\
\]

- On the other hand, ammonia is a base because it increases the concentration of $OH^-$:

\[
NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \\
\]
Solvent System Model

Many solvents dissociate to some degree:

\[
2H_2O \quad \underset{pK_{\text{ion}} = 14.0}{\overset{pK_{\text{ion}}}{\rightleftharpoons}} \quad H_3O^+ + OH^- \\
pK_{\text{ion}} = -\log K_{\text{ion}} = -\log([H_3O^+][OH^-])
\]

\[
2H_2SO_4 \quad \underset{pK_{\text{ion}} = 3.4 (10^\circ C)}{\overset{pK_{\text{ion}}}{\rightleftharpoons}} \quad H_3SO_4^+ + HSO_4^- \\
2NH_3 \quad \underset{pK_{\text{ion}} = 27}{\overset{pK_{\text{ion}}}{\rightleftharpoons}} \quad NH_4^+ + NH_2^- \\
2CH_3CN \quad \underset{pK_{\text{ion}} = 34.4}{\overset{pK_{\text{ion}}}{\rightleftharpoons}} \quad CH_3CNH^+ + CH_2CN^- 
\]
The Lewis Concept

A base is an electron-pair donor and an acid is an electron-pair acceptor

- This model is consistent with the Arrhenius and Brønsted-Lowry Models:

\[ H^+ + :NH_3 \rightarrow NH_4^+ \]

Lewis  Lewis
Acid    Base

- It also works with molecules that neither give up nor accept a hydrogen ion

\[ BF_3 + :NH_3 \rightarrow H_3N : BF_3 \]

Lewis  Lewis  Lewis
Acid    Base    Adduct
The Lewis Concept

The Lewis concept also allows us to describe coordination complexes within an acid-base framework.

Ag⁺ + 2 :NH₃ → H₃N⁺Ag⁻⁻NH₃

Coordinate covalent or dative bond – used to show that both electrons in the bond come from a Lewis base

• Lewis Acid-Base adducts in which the Lewis acid is a metal ion are typically called coordination compounds
The Lewis Concept and Molecular Orbitals

The Lewis concept of acids and bases is readily interpreted using molecular orbital theory.

\[ BF_3 + :NH_3 \rightarrow H_3N : BF_3 \]

An acid-base reaction occurs when HOMO of the base and LUMO of the acid combine to create new HOMO and LUMO in the product.
The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

Here, water acts as an “extreme Lewis acid” to oxidize Ca to Ca\(^{2+}\) (complete electron transfer)

\[ 2 \text{H}_2\text{O} + \text{Ca} \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- + \text{H}_2 \]
The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

Here, water acts as a Lewis acid to form an adduct with an anion

\[ n \text{H}_2\text{O} + \text{Cl}^- \rightarrow [\text{Cl(H}_2\text{O})_n^-] \]
The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

Here, water acts as a Lewis base to form an adduct with a metal cation

\[
6 \text{H}_2\text{O} + \text{Mg}^{2+} \rightarrow [\text{Mg(H}_2\text{O})_6]^{2+}
\]
The MO perspective on Lewis acids/bases is versatile and can help us understand many types of reactions. Consider water:

Here, water acts as an “extreme Lewis base” to reduce F₂ to 2 F⁻ (complete transfer)

\[ 2 \text{H}_2\text{O} + 2 \text{F}_2 \rightarrow 4 \text{F}^- + 4 \text{H}^+ + \text{O}_2 \]
The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- hard Lewis acids are small acids with a high positive charge
- soft Lewis acids are larger and typically have a lower positive charge

<table>
<thead>
<tr>
<th>Hard Acids</th>
<th>Borderline Acids</th>
<th>Soft Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H^+ ), ( Li^+ ), ( Na^+ ), ( K^+ )&lt;br&gt;( Be^{2+} ), ( Mg^{2+} ), ( Ca^{2+} ), ( Sr^{2+} )&lt;br&gt;( BF_3 ), ( BCl_3 ), ( B(OR)_3 )&lt;br&gt;( Al^{3+} ), ( AlCl_3 ), ( AlH_3 )&lt;br&gt;( Cr^{3+} ), ( Mn^{2+} ), ( Fe^{3+} ), ( Co^{3+} )&lt;br&gt;( Mn^{n+} ) ( (n \geq 4) )&lt;br&gt;H-bonding molecules</td>
<td>( B(CH_3)_3 )&lt;br&gt;( Fe^{2+} ), ( Co^{2+} ), ( Ni^{2+} )&lt;br&gt;( Cu^{2+} ), ( Zn^{2+} )&lt;br&gt;( Rh^{3+} ), ( Ir^{3+} ), ( Ru^{3+} ), ( Os^{2+} )</td>
<td>( BH_3 ), ( Ti^+ ), ( Ti(CH_3)_3 )&lt;br&gt;( Cu^+ ), ( Ag^+ ), ( Au^+ ), ( Cd^{2+} )&lt;br&gt;( Hg_2^{2+} ), ( Hg^{2+} ), ( CH_3Hg^+ )&lt;br&gt;[( Co(CN)_5 )]^{2–} ( , Pd^{2+} ), ( Pt^{2+} )&lt;br&gt;( Br_2 ), ( I_2 )&lt;br&gt;( Mn^{n+} ) ( (n = 0) )&lt;br&gt;( \pi )-acceptor molecules</td>
</tr>
</tbody>
</table>
The Hard-Soft Acid-Base (HSAB) concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- **Hard Lewis Bases** are small bases with highly electronegative donor atoms.
- **Soft Lewis Bases** are larger and typically have smaller electronegativities.

### Table: HSAB Model

<table>
<thead>
<tr>
<th>Hard Bases</th>
<th>Borderline Bases</th>
<th>Soft Bases</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(^{-}), Cl(^{-})</td>
<td>Br(^{-}) NO(_2)(^{-}), N(_3)(^{-}) SO(_3)(^2)(^{-}) C(_6)H(_5)NH(_2), C(_5)H(_5)N, N(_2)</td>
<td>H(^{-}) I(^{-}) H(_2)S, SH(^{-}), S(^2)(^{-}), RSH, RS(^{-}), R(_2)S SCN(^{-}), CN(^{-}), RNC, CO S(_2)O(_3)(^2)(^{-}) PR(_3), P(OR)(_3), AsR(_3), C(_2)H(_4), C(_6)H(_6), R(^{-})</td>
</tr>
<tr>
<td>H(_2)O, OH(^{-}), O(^2)(^{-}), ROH, RO(^{-}), R(_2)O, RCOO(^{-}) NO(_3)(^{-}), ClO(_4)(^{-}), CO(_3)(^2)(^{-}) SO(_4)(^2)(^{-}), PO(_4)(^3)(^{-}) NH(_3), RNH(_2), N(_2)H(_4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The Hard-Soft Acid-Base concept seeks to understand the reactivity of Lewis acids and bases according to the polarizability of their valence electrons (i.e., their deformability by other molecules/ions).

- hard Lewis acids are small acids with a high positive charge, soft Lewis acids are larger and typically have a lower positive charge
- hard Lewis bases are small bases with electronegative donor atoms, soft Lewis bases are larger and typically have smaller electronegativities

Hard acids prefer to interact with hard bases, soft acids prefer to interact with soft bases.

\[ \text{ZnO} + 2\text{LiC}_4\text{H}_9 \rightarrow \text{Zn} \left( \text{C}_4\text{H}_9 \right)_2 + \text{Li}_2\text{O} \]

borderline acid    hard acid    borderline acid    hard acid
hard base          soft base    soft base          hard base
HSAB theory is consistent with the large differences in $K_{eq}$ for simple exchange reactions:

**TABLE 6.3 Equilibrium Constants for Reactions of Mercury Complexes$^{25}$**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $[\text{CH}_3\text{Hg(H}_2\text{O)}]^+ + \text{HF} \rightleftharpoons \text{CH}_3\text{HgF} + \text{H}_3\text{O}^+$</td>
<td>$4.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>2. $[\text{CH}_3\text{Hg(H}_2\text{O)}]^+ + \text{HCl} \rightleftharpoons \text{CH}_3\text{HgCl} + \text{H}_3\text{O}^+$</td>
<td>$1.8 \times 10^{12}$</td>
</tr>
<tr>
<td>3. $[\text{CH}_3\text{Hg(H}_2\text{O)}]^+ + \text{HBr} \rightleftharpoons \text{CH}_3\text{HgBr} + \text{H}_3\text{O}^+$</td>
<td>$4.2 \times 10^{15}$</td>
</tr>
<tr>
<td>4. $[\text{CH}_3\text{Hg(H}_2\text{O)}]^+ + \text{HI} \rightleftharpoons \text{CH}_3\text{Hgl} + \text{H}_3\text{O}^+$</td>
<td>$1 \times 10^{18}$</td>
</tr>
</tbody>
</table>

Hg$^{2+}$ is a soft acid. As the halide becomes softer, the reaction becomes increasingly favorable.
HSAB Theory and Solubilities

Because the dissolution of salts in water typically requires the replacement of a Lewis base with water, HSAB can predict trends in solubilities. Consider the silver halides:

\[ \text{AgX}(s) \xrightleftharpoons[H_2O]{} \text{Ag}(aq)^+ + X(aq)^- \]

\[ X = F \gg Cl > Br > I \]

- F\(^-\) and Cl\(^-\) are hard bases; however, so is water. It turns out that water is softer than F\(^-\) but harder than Cl\(^-\).
- Br\(^-\) and I\(^-\) are soft bases.
- Because Ag\(^+\) is a soft acid, it is less prone to give up the halide as we move down the series.
Because the dissolution of salts in water typically requires the replacement of a Lewis base with water, HSAB can predict trends in solubilities. Lithium halides show the opposite trend:

\[ \text{LiX(s)} \rightleftharpoons \text{Li}^{+}(aq) + X^{-}(aq) \]

\[ X = F \ll Cl < Br < I \]

- F\(^{-}\) and Cl\(^{-}\) are hard bases; however, so is water. It turns out that water is softer than F\(^{-}\) but harder than Cl\(^{-}\).
- Br\(^{-}\) and I\(^{-}\) are soft bases.
- In this case, Li\(^{+}\) is a hard acid and it prefers to interact with the hardest base available.
In coordination complexes the metal is the Lewis acid. The Lewis base is normally called a *ligand*.

- Thiocyanate (SCN⁻) is an interesting ligand because there are two Lewis base sites:

```
Θ S-C≡N : ← linkage isomerism → S=C≡N Θ
```

```
Hg²⁺ \[\text{NCS} \cdots \text{Hg} \cdots \text{SCN}\]^{2−}
```

```
Zn²⁺ \[\text{SCN} \cdots \text{Zn} \cdots \text{NCS}\]^{2−}
```
Pearson’s Absolute Hardness Scale

The absolute hardness is defined as

\[ \eta = \frac{I - A}{2} \]

- \( I \) is the ionization energy of the molecule in eV, approximately equal to \(-E_{\text{HOMO}}\)
- \( A \) is the electron affinity of the molecule in eV, approximately equal to \(-E_{\text{LUMO}}\)
- So the absolute hardness is just half the HOMO-LUMO difference (i.e., half the band gap!)

- Hard acids have large values for \( \eta \), soft acids have smaller values for \( \eta \)
- Softness of a donor atom is given by the inverse of hardness, i.e.,

\[ \sigma = \frac{1}{\eta} \]
Pearson’s Absolute Hardness Scale

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ion</th>
<th>Parameter</th>
<th>Parameter</th>
<th>Parameter</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al^{3+}</td>
<td></td>
<td>119.99</td>
<td>28.45</td>
<td>74.22</td>
<td>45.77</td>
</tr>
<tr>
<td>Li^{+}</td>
<td></td>
<td>75.64</td>
<td>5.39</td>
<td>40.52</td>
<td>35.12</td>
</tr>
<tr>
<td>Na^{+}</td>
<td></td>
<td>47.29</td>
<td>5.14</td>
<td>26.21</td>
<td>21.08</td>
</tr>
<tr>
<td>K^{+}</td>
<td></td>
<td>31.63</td>
<td>4.34</td>
<td>17.99</td>
<td>13.64</td>
</tr>
<tr>
<td>Au^{+}</td>
<td></td>
<td>20.5</td>
<td>9.23</td>
<td>14.90</td>
<td>5.60</td>
</tr>
<tr>
<td>BF_{3}</td>
<td></td>
<td>15.81</td>
<td>-3.5</td>
<td>6.2</td>
<td>9.7</td>
</tr>
<tr>
<td>H_{2}O</td>
<td></td>
<td>12.6</td>
<td>-6.4</td>
<td>3.1</td>
<td>9.5</td>
</tr>
<tr>
<td>NH_{3}</td>
<td></td>
<td>10.7</td>
<td>-5.6</td>
<td>2.6</td>
<td>8.2</td>
</tr>
<tr>
<td>PF_{3}</td>
<td></td>
<td>12.3</td>
<td>-1.0</td>
<td>5.7</td>
<td>6.7</td>
</tr>
<tr>
<td>PH_{3}</td>
<td></td>
<td>10.0</td>
<td>-1.9</td>
<td>4.1</td>
<td>6.0</td>
</tr>
<tr>
<td>F^{-}</td>
<td></td>
<td>17.42</td>
<td>3.40</td>
<td>10.41</td>
<td>7.01</td>
</tr>
<tr>
<td>Cl^{-}</td>
<td></td>
<td>13.01</td>
<td>3.62</td>
<td>8.31</td>
<td>4.70</td>
</tr>
<tr>
<td>Br^{-}</td>
<td></td>
<td>11.84</td>
<td>3.36</td>
<td>7.60</td>
<td>4.24</td>
</tr>
<tr>
<td>I^{-}</td>
<td></td>
<td>10.45</td>
<td>3.06</td>
<td>6.76</td>
<td>3.70</td>
</tr>
</tbody>
</table>

NOTE: The anion values are approximated as the same as the parameters for the corresponding neutral radicals or atoms.
Hard acid/hard base adducts tend to have more ionic character in their bonding. These are generally more favored energetically.

Soft acid/soft base adducts are more covalent in nature.
It is important to realize that hard/soft considerations have nothing to do with acid or base strength. An acid or a base may be hard or soft and also be either weak or strong.

In a competition reaction between two bases for the same acid, one must consider both the relative strength of the bases, and the hard/soft nature of each base and the acid.

\[
\text{ZnO} + 2\text{LiC}_4\text{H}_9 \rightarrow \text{Zn(C}_4\text{H}_9)_2 + \text{Li}_2\text{O}
\]

Zinc ion is a strong Lewis acid, and oxide ion is a strong Lewis base, suggesting the reaction is unfavorable as written.

However, the reaction proceeds to the right \((K > 1)\), because hard/soft considerations override acid-base strength considerations.
Drago’s EC Approach

A quantitative system for calculating the thermodynamics of acid-base reactions takes account of both covalent and ionic components of the acid-base interaction. For the reaction,

\[ A + B \xrightleftharpoons{\Delta H} AB \]

\[-\Delta H = E_A E_B + C_A C_B\]

- \( E_A \) and \( E_B \) are the capacity for electrostatic (ionic) interactions of the acid and base
- \( C_A \) and \( C_B \) are the capacity for covalent interactions of the acid and base
- \( I_2 \) is the reference acid with \( C_A = E_A = 1.00 \text{ kcal/mol} \)
- Reference bases are MeC(O)NMe\(_2\) (\( E_B = 1.32 \)) and SEt\(_2\) (\( C_B = 7.40 \))
Using the EC Model

The enthalpy of a given Lewis acid-base reaction can be determined using tabulated values (see Table 6.17 in your textbook).

\[ I_2 + C_6H_6 \rightleftharpoons I_2 \cdot C_6H_6 \]

\[
-\Delta H = E_A E_B + C_A C_B
\]

\[
-\Delta H = \left( 1.00 \frac{kcal}{mol} \right) \left( 0.525 \frac{kcal}{mol} \right) + \left( 1.00 \frac{kcal}{mol} \right) \left( 0.681 \frac{kcal}{mol} \right)
\]

\[ \Delta H = -1.21 \frac{kcal}{mol} \] within 9% of experimental value
Summary

- There are several models to describe acids and bases. The Lewis model is one of the most general since it does not depend on the transfer of a hydrogen ion.

- A dative bond (coordinate covalent bond) is often used to denote a bond between a neutral Lewis base and a Lewis acid:

\[
\text{H}_3\text{N} \rightarrow \text{BF}_3
\]

- The Lewis model is readily interpreted using MO theory: the HOMO of the Lewis base interacts with the LUMO of the Lewis acid.

- HSAB provides a semi-quantitative method for understanding trends in acid-base reactivity: hard acids like hard bases and soft acids like soft bases.

- The Drago EC model provides a more quantitative method for understanding the thermodynamics of an acid-base reaction.